

Laurates and Pelargonates of Lactic Esters as Plasticizers for Vinyl Resins

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PLASTICIZERS are a necessary component for the fabrication and use of numerous items manufactured from plastics. The tremendous growth in recent years in the applications of plastics, particularly vinyl chloride resins, has been accompanied by an increasing demand for plasticizers (1)³. The demand for plasticizers has exceeded the supply, and critical shortages have been felt (1, 2). Plasticizers currently available, furthermore, do not satisfy in every respect the specifications required in some applications (2, 3). As a result, extensive research for new plasticizers and for new sources of raw materials for this rapidly growing organic chemical industry has been undertaken (4, 5, 6, 7).

The properties desirable in a plasticizer for vinyl chloride resins have been discussed recently (8, 9, 10). The advantages of lactic acid as a raw material for preparing plasticizers were pointed out in an earlier publication from this Laboratory (11). In the past few years, preparation of a number of high-boiling esters of lactic acid of potential value as plasticizers has been reported. Since lactic acid contains both a carboxyl and hydroxyl group, a variety of derivatives containing multiple ester groups can be prepared. Derivatives such as the diethylene glycol bis-carbonates (11), alkyl carbonates (12), adipates, sebacates, phthalates, and maleates (13) of lactic esters and esters of polymeric lactic acid (14) have been prepared and screened as plasticizers, particularly for the 95% vinyl chloride copolymer. Some showed properties as plasticizers which merit interest in this application.

This paper reports the preliminary evaluation of pelargonates and laurates of various lactic esters as plasticizers, and a study of the esterification reaction between butyl lactate and lauric acid as a method of preparation of this type derivative. Esterification with pelargonic acid presumably would be comparable to esterification with lauric acid.

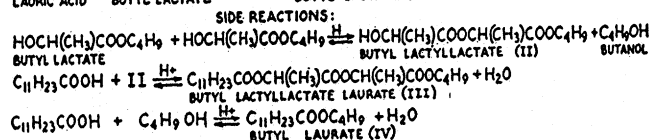
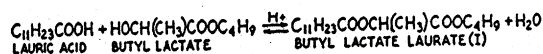
Preparation of Mixed Esters of Lactic and Fatty Acids

The pure ester derivatives of lactic and fatty acids, corresponding to the formula $\text{RCOOCH}(\text{CH}_2)_n\text{COOR}'$, were prepared by acylating the appropriate lactic ester with a fatty acid chloride, as described previously (15,

16, 17). For purposes of comparison, n-butyl, benzyl, and tetrahydrofurfuryl laurates were also investigated.

Direct Esterification of Lactic Esters with Lauric Acid

Because n-butyl lactate laurate appears to be one of the promising derivatives, its preparation by an esterification process was investigated in detail. Lactic esters, containing a hydroxyl group in addition to the ester group, are capable of direct esterification, as demonstrated in an earlier paper (18). The esterification, however, is not so simple as the esterification of an acid with a simple alcohol. Complications by side reactions such as the self-alcoholysis of the lactic ester (to produce an alcohol and lactyllactate) and subsequent esterification of these side products are encountered. These reactions are illustrated by the equations below. In the esterification reaction all the products corresponding to I-IV in the equations were produced; however, these were readily separable by distillation in vacuum.



The esterification was conducted in the presence of an entraining agent, usually toluene, to remove water from the reaction mixture. A typical example follows: A mixture of butyl lactate (146 grams, 1.0 mole), lauric acid (100 grams, 0.5 mole), toluene (100 milliliters) and p-toluenesulfonic acid monohydrate (1.0 gram) was placed in a flask attached to a modified Dean and Stark tube for collection of the water from the reaction. The mixture was refluxed until the amount of water collected in the trap approached the theoretical quantity. The contents of the flask were agitated by boiling or by means of a magnetic stirrer.

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³ Numbers in parentheses refer to Bibliography items at the end of the article.

In general, the free acid content of the esterification mixture was reduced to approximately 1% (as lauric acid). The catalyst was then neutralized with a slight excess of anhydrous sodium acetate or calcium lactate, and the reaction mixture was distilled in vacuum through a two-foot Vigreux column. The entraining agent was removed at a pressure of approximately 40 millimeters of mercury, and the higher boiling fractions at two to five millimeters of mercury pressure. The products isolated were unreacted butyl lactate (0.46 mole), butyl lactyllactate (0.1 mole), butyl laurate (0.25 mole), butyl lactate laurate (0.23 mole), and distillation residue (11 grams). The distillation residue was principally butyl lactyllactate laurate.

Table 1 summarizes the esterification of n-butyl lactate, sec-butyl lactate, and capryl lactate with lauric acid. Under the conditions of Experiments 6, 8, and 9 in Table 1, approximately 50% of the lauric acid was converted into butyl lactate laurate. Capryl lactate was more suitable than butyl lactate; 66% of the lauric acid was converted into capryl lactate laurate.

TABLE 1. DIRECT ESTERIFICATION OF LACTIC ESTERS WITH LAURIC ACID

Expt. No.	Lactic Ester, Moles	Mole Ratio*	Catalyst, Gram	Entrainer†	Reaction Temp., °C.	Reaction Time, Hrs.	H ₂ O, Ml.	Products, % Conversion		
								Lactyl-lactate‡	Alkyl Laurate§	Lactate Laurate§
1	n-Butyl lactate, 3.0	3.0	None	Butyl lactate	184-191	13.3	15.5	26	47	26
2	n-Butyl lactate, 3.0	3.0	TSA(¶), 0.1	Butyl lactate	184-196	10.9	17.1	25	52	37
3	n-Butyl lactate, 1.0	2.0	TSA(¶), 1.0	Butyl lactate	205-239	2.4	7.6	22	57	32
4	n-Butyl lactate, 1.0	2.0	TSA(¶), 1.0	Benzene	110-120	5.2	8.4	23	49	40
5	n-Butyl lactate, 1.0	2.0	TSA(¶), 0.1	Toluene	150-153	9.9	ca. 6.0	18	18	38
6	n-Butyl lactate, 1.0	2.0	TSA(¶), 1.0	Toluene	140-150	2.2	9.0	16	47	46
7	n-Butyl lactate, 1.0	2.0	TSA(¶), 4.0	Toluene	130-142	1.0	9.0	22	54	22
8	n-Butyl lactate, 1.0	2.0	H ₂ SO ₄ , 0.25	Toluene	148	9.0	7.8	16	32	48
9	n-Butyl lactate, 1.0	2.0	TSA, 1.0	Benzene	120-133	5.1	8.6	20	30	52
10	n-Butyl lactate, 1.0	2.0	TSA, 1.0	Toluene	146-157	3.0	9.0	26	14	44
11	sec-Butyl lactate, 0.87	1.7	TSA, 1.0	Toluene	140-142	2.5	9.2	15	24	22
12	Capryl lactate, 1.0	2.0	TSA, 1.0	Toluene	141-153	3.5	8.5	66

*Ratio of lactic ester to lauric acid.

†100 milliliters benzene or toluene were used.

‡Based on lactic ester.

perature to 124-180° C., gave only a 26% yield of butyl lactate laurate. Generally speaking, the ester interchange process was not so satisfactory as the direct esterification process.

Esterification Procedure with Recycling of By-Products

It was evident from the study of the esterification of butyl lactate with lauric acid that a mixture of esters, that is, butyl lactyllactate, butyl laurate, butyl lactate laurate, and butyl lactyllactate laurate, was produced. The latter two are high-boiling esters collected as the last fractions in the distillation. The mixture of these two may be considered a plasticizer. The by-products of the esterification reaction then would be butyl lactyllactate and butyl laurate, which are the most volatile products. These were removed by distillation from the mixture and recycled in the esterification of butyl lactate with lauric acid. The distillation residue is composed of a mixture of butyl lactate laurate and butyl lactyllactate laurate.

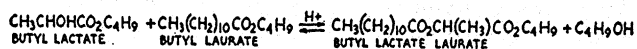
§Based on lauric acid.

¶TSA—p-toluenesulfonic acid monohydrate.

||In addition, 0.5-mole of butyl laurate was included in the reaction mixture.

Butyl Lactate Laurate by Ester Interchange

In addition to the esterification process described above, butyl lactate laurate may also be prepared by ester interchange from butyl lactate and butyl laurate as shown in the following equation:



As in the direct esterification, this process is also complicated by side reactions; the by-products are essentially derivatives of polymeric lactic acid.

A mixture of n-butyl lactate (0.5 mole), n-butyl laurate (1.0 mole), and 3.0 grams of p-toluenesulfonic acid was refluxed under a Vigreux column; the contents of the flask were stirred by means of a magnetic stirrer. Butanol was distilled from the reaction mixture as formed, and the vapor temperature was maintained at 110-116° C.

In approximately three hours the reaction temperature rose to about 285° C., and the theoretical amount (0.5 mole) of butanol was collected. The ester interchange catalyst was then neutralized by adding a slight excess of calcium lactate or sodium acetate, and the reaction mixture was distilled in vacuum. Sixty-eight per cent. of the butyl laurate and a trace of the butyl lactate were recovered unchanged. The yield of butyl lactate laurate was 48%. An experiment in which the mole ratio of butyl laurate to butyl lactate was 4:1 gave a 60% yield of lactate laurate.

An experiment similar to the above except that the ester interchange was conducted at a pressure of 50 millimeters of mercury, thus reducing the reaction tem-

A series of experiments was conducted according to the general procedure described for butyl lactate laurate. In each experiment, one mole of butyl lactate and 0.5 mole of lauric acid were used, and the ratio of catalyst and entraining agent to the total amount of other reactants was maintained constant. After the esterification was complete, the catalyst was neutralized as before, and the mixture was distilled. Unreacted butyl lactate, boiling at 40° C. at one millimeter of mercury pressure, butyl lactyllactate, boiling at 91-105° C. at 1.2 millimeters of mercury pressure, and butyl laurate, boiling at 115-120° C. at one millimeter of mercury pressure were removed. The residual material was the plasticizer mixture containing the lactate laurate and lactyllactate laurate esters. The butyl lactyllactate and butyl laurate obtained from the run were added to the next esterification batch, and this recycling process was continued through a total of six cycles. The results are tabulated in Table 2.

TABLE 2. ESTERIFICATION OF BUTYL LACTATE WITH LAURIC ACID—RECYCLING EXPERIMENTS

Composition of Reaction Mixture	Cycle					
	1	2	3	4	5	6
n-Butyl lactate, g.	146	146	146	146	146	146
Lauric acid, g.	100	100	100	100	100	100
n-Butyl laurate, g.	...	76	139	170	222	252
n-Butyl lactyllactate, g.	...	28	40	58	62	49
p-Toluenesulfonic acid, g.	1	1.4	1.70	1.9	2.15	2.22
Toluene, ml.	100	140	170	190	215	222
Conditions						
Temperature, °C.	135-144	137-145	142-145	135-144	142-145	141-145
Time, hrs.	2.5	3.2	2.5	3	3	4
Products recovered						
n-Butyl lactate, g.	46	55	66	53	78	61
n-Butyl laurate, g.	76	139	170	222	252	256
n-Butyl lactyllactate, g.	28	40	58	62	49	63
n-Butyl lactate laurate mixture, g.*	78	96	104	114	115	138

*Recovered as a distillation residue.

TABLE 3. PELARGONATES AND LAURATES OF LACTIC ESTERS AS PLASTICIZERS

Plasticizer	B. P.		Compatibility*		Properties of Plasticized VYDR Composition§			
	°C.	Mm. Hg.	Unaged†		Tensile P.S.I.	100% Modulus P.S.I.	Elongation %	Brittle Point, °C.
			Unaged†	Aged‡				
1-Butyl lactate pelargonate.....	143	3.0	CI	CI	3550	1700	250	-39
n-Butyl lactate laurate.....	180	4.0	CI	CI	2520	1170	330	-67
Iso-Butyl lactate laurate.....	179	4.0	CI	CI	2630	1220	280	-51
Sec-Butyl lactate laurate.....	176	4.0	CI	CI	2920	1270	340	-62
2-Ethylhexyl lactate laurate.....	207	4.0	I
Capryl lactate laurate.....	182	0.8	I
4-Methyl-2-pentyl lactate laurate.....	187	4.0	C	CI	3040	1320	350	-42
Cyclohexyl lactate laurate.....	205	4.0	CI	I	3130	1380	300	-46
Benzyl lactate laurate.....	217	4.0	CI	I	2850	1240	320	-59
2-Ethoxyethyl lactate laurate.....	193	4.0	I	...	2350	1310	240	-44
2-Butoxyethyl lactate laurate.....	204	3.2	I	...	2990	1110	350	-46
2-Chloroethoxyethyl lactate pelargonate.....	183	4.0	CI	I	2670	910	330	-33
Tetrahydrofurfuryl lactate heptanoate.....	171	5.4	C	I	2930	1060	340	-32
Tetrahydrofurfuryl lactate pelargonate.....	202	10.0	C	I	2780	1110	340	-42
Tetrahydrofurfuryl lactate laurate.....	211	4.0	C	I
2-(2-Ethoxyethoxy) ethyl lactate laurate.....	189	1.0	CI	CI	2560	1110	320	-56
2-(2-Butoxyethoxy) ethyl lactate pelargonate.....	195	4.0	I	CI	2720	1380	270
Laurate.....	229	4.0	C	I	2720	1150	325	-44
Ethyl lactyl lactate laurate.....	171	0.9	C	I	3090	1400	200	-52
n-Butyl lactyl lactate laurate.....	188	1.2	C	I
n-Butyl laurate.....	150	4.0	I	...	3000	1230	320
Benzyl laurate.....	189	4.0	I	...	2540	920	320	-58
Tetrahydrofurfuryl laurate.....	178	4.0	C	I	3150	1500	320	-32
DOP (control).....	228	4.0	C	C	3475	2200	280	-5
Tricresyl phosphate (control).....	233	2.0	C	C

*C—compatible; I—incompatible; CI—borderline compatibility.

†Molded composition after conditioning at 70° F. for 24 to 48 hours.

‡After several months under room conditions.

§Contained 35% plasticizer.

It can be seen that the yield of the mixture of lactate laurates is considerably improved by recycling the butyl lactyl lactate and butyl laurate. Although an absolutely steady state had not been reached in six cycles, it appears that this condition had been approximated by the fourth cycle. The amount of butyl laurate and lactyl lactate obtained in the fifth or sixth cycles was approximately equal to the input of these two materials.

The undistilled mixture of lactate laurates can be easily distilled at one millimeter of mercury pressure to give an almost colorless product. Decolorizing carbon was not completely satisfactory for color removal. Esterification in which ion exchange resins: namely, Zeo-Karb H⁴ and Permutit Q,⁴ were used as catalysts resulted in a lighter-colored product, but the time required for complete esterification was considerably longer.

Analysis by distillation of a typical lactate laurate esterification mixture showed that it contained 63% by weight of butyl lactate laurate, 26% of butyl lactyl lactate laurate, and 11% of higher boiling esters of polylactic acid.

Evaluation as Plasticizers

These derivatives were screened as plasticizers for Vinylite VYDR,⁴ a 95% vinyl chloride 5% vinyl acetate copolymer. The plasticizer was milled into the resin according to the procedure described in a technical bulletin (19). The formulation used was:

	Parts
Polyvinyl chloride (VYDR)	63.5
Basic lead carbonate	1.0
Stearic acid	0.5
Plasticizer	35.0

The molded sheets (6.0 by 6.0 by 0.08 inches) were conditioned for 24-48 hours at 77° F. and 50% relative humidity. Compatibility was determined by the appearance of the sheet at this stage. Dumbell test specimens with necks 0.125-inch wide and one inch long in the straight portion were die-cut from the molded sheet, and conditioned for one hour at 70° F. and 65% relative humidity. The tensile strength, 100% modulus, and elongation were determined (70° F., 65% relative humidity). A Scott IP-4 tester was used, and the rate of load application was 73 pounds per minute. Specimens,

⁴ Mention of any specific brand names is not to be construed as an endorsement or recommendation by the Department of Agriculture.

¼ by 1½ inches, were cut from the molded sheet for determination of the brittle point, as described by other workers (20). After the molded sheets were kept under room conditions for several months, they were also examined for exudation. The results are summarized in Table 3.

Several of the lactate laurates appeared to be compatible upon first examination, but a slight bloom developed on the surface after the sample was several months old. The laurates of the butyl and cyclohexyl lactates appeared to be of borderline compatibility at 35% concentration. One interesting feature of the data of Table 3 is the low brittle points of the compositions plasticized with these lactate laurates, as compared with the control, DOP.

TABLE 4. ACYLATED LACTIC ESTER-DOP BLENDS (50-50) AS PLASTICIZERS

Acylated Lactic Ester	Compatibility*		Properties of Plasticized VYDR Composition§			
	Unaged†	Aged‡	Tensile P.S.I.	100% Modulus P.S.I.	Elongation %	Brittle Point, °C.
n-Butyl lactate laurate	C	CI	2340	1190	160	-44
Sec-Butyl lactate laurate	C	C	2980	1240	300	-45
2-Ethylhexyl lactate laurate	C	CI	2920	1390	320	-53
Capryl lactate laurate	C	C	2840	1450	230	-55
4-Methyl-2-pentyl lactate laurate	C	C	3050	1370	280	-48
Benzyl lactate laurate	C	C	2990	1180	300	-38
2-Ethoxyethyl lactate laurate	C	CI	2940	1300	320	-41
2-Butoxyethyl lactate laurate	C	CI	3090	1300	330	-46
2-Chloroethoxyethyl lactate pelargonate	C	CI	2980	1180	320	-42
Tetrahydrofurfuryl lactate pelargonate	C	C	3450	1760	290	-30
Laurate	C	CI	2970	1260	350	-38
2-(2-Butoxyethoxy) ethyl lactate pelargonate	C	CI	2520	1170	210	-44
Laurate	CI	I	3040	1340	350	-37
DOP	C	C	3150	1500	320	-32

*C—compatible; I—incompatible; CI—borderline compatibility.

†After conditioning for 24-48 hours.

‡After several months under room conditions.

§Total plasticizer concentration—35%.

Since the lactate laurates do not appear suitable as primary plasticizers, it was of interest to investigate blends of these with common plasticizers such as di-2-ethylhexyl phthalate and tricresyl phosphate. Table 4 shows the data for 50% blends of various lactate laurates with DOP. As expected, the compatibility of the lactate laurates was decidedly improved. Of the DOP blends examined, those containing the laurates of capryl, 4-

methyl-2-pentyl (methyl isobutyl carbonyl), and benzyl lactates appeared to be compatible, and, as judged from the 100% modulus, they were comparable in efficiency with DOP alone. The brittle points of the plasticized compositions containing the blends were 6° to 23° C. lower than the brittle points of DOP, which was the control.

Table 5 shows the results obtained with 50% blends of several lactate laurates with tricresyl phosphate. When blended with tricresyl phosphate, all the lactate laurates examined were compatible at 35% concentration in the plastic. Tricresyl phosphate appeared to be more effective than DOP in compatibilizing these derivatives. As judged by the 100% modulus and brittle point of the compositions, these blends, except those containing the laurates of benzyl lactate and butyl lactyl lactate, were approximately equivalent to DOP in plasticizing efficiency.

TABLE 5. LACTATE LAURATE-TRICRESYL PHOSPHATE BLENDS (50-50) AS PLASTICIZERS

Lactate Laurate	Properties of Plasticized VYDR Composition*			
	Tensile, P.S.I.	100% Modulus, P.S.I.	Elongation, %	Brittle Point, °C.
n-Butyl lactate laurate.....	3055	1170	335	-41
Sec-Butyl lactate laurate.....	3170	1325	290	-42
Iso-Butyl lactate laurate.....	3105	1370	295	-39
4-Methyl 2-pentyl lactate laurate.....	3365	1555	280	-40
2-Ethoxyethyl lactate laurate.....	3200	1330	285	-38
Benzyl lactate laurate.....	3560	1680	300	-20
Cyclohexyl lactate laurate.....	3265	1485	305	-27
n-Butyl lactyl lactate laurate.....	3340	1760	265	-11
Controls				
Benzyl laurate+TCP (50-50).....	3090	1185	290	-42
Tetrahydrofurfuryl laurate+TCP.....	3185	1275	230	-34
TCP (tricresyl phosphate).....	3475	1945	280	-5
DOP (50-50).....	3325	1545	290	-22
DOP (dioctyl phthalate).....	3200	1320	320	-32

*All plasticizer blends were compatible in both unaged and aged compositions.

TABLE 6. BUTYL LACTATE LAURATE MIXTURE AS PLASTICIZER*

Plasticizer	% by Weight	Properties of Plasticized VYDR Composition				
		Compatibility†		Tensile, P.S.I.	100% Modulus, P.S.I.	Elongation, %
Butyl lactate laurate mixture*.....	35	Unaged	Aged	2770	1185	400
Butyl lactate laurate mixture+TCP (50-50).....	30	C	†	3310	1750	290
DOP (50-50).....	35	C	C	3240	1230	350
DOP.....	35	C	C	2905	1195	350
Tricresyl phosphate.....	30	C	C	3075	1260	400
	35	C	C	3650	2100	290
	35	C	C	3475	1945	280

*The mixture of butyl lactate laurate and butyl lactyl lactate laurate obtained in the recycling esterification of butyl lactate with lauric acid.

†C-compatible. Aged refers to composition after more than four months at room temperature. Unaged refers to composition after conditioning for 24-48 hours.

‡Slight bloom.

Because esterification of butyl lactate with lauric acid produced a mixture of butyl lactate laurate and butyl lactyl lactate laurate, this mixture of lactate laurates was investigated as a plasticizer for the vinyl chloride copolymer. The data are summarized in Table 6. This mixture was of borderline compatibility when used alone to the extent 35% by weight of the composition; however, at 30% concentration it appeared entirely compatible.

The composition with 30% plasticizer showed a lower brittle point (-45° C.), but a higher modulus than the control (35% DOP). The 50-50 blend of this

mixture with tricresyl phosphate appeared to be equivalent to DOP in plasticizing efficiency; whereas the 50-50 blend of this mixture with DOP was judged to be superior to DOP alone.

Summary and Conclusions

Pelargonates and laurates of various lactic esters were evaluated in respect to their efficiency as plasticizers for the vinyl resins. When used at 35% concentration in the plastic, these derivatives were not suitable as primary plasticizers. When used as blends with dioctyl phthalate or tricresyl phosphate, these derivatives showed desirable plasticizing properties, particularly low-temperature properties. Esterification of butyl lactate with lauric acid was also studied, and conditions were found which produced a mixture of butyl lactate laurate and butyl lactyl lactate laurate in high yield. This mixture was in several respects more desirable as a plasticizer than either of the pure components. The lactate laurates may be of interest for use in plasticizer blends with dioctyl phthalate or tricresyl phosphate, particularly for improving the low-temperature properties of these two.

The authors are indebted to W. E. Palm and H. C. Fromuth for assistance in evaluating these materials.

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